

## ZnS-based photonic crystal phosphors fabricated using atomic layer deposition

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The infiltration by atomic layer deposition of three-dimensional opal structures has been investigated as a means of fabricating photonic crystal phosphors. ZnS:Mn infiltrated and inverse opals have been demonstrated with filling fractions >95%. Characterization of these structures by scanning electron microscopy, specular reflectance, and photoluminescence is reported. Specular reflectance measurements confirm successful infiltration, and demonstrate modification of the electromagnetic density of states consistent with calculated photonic (111) pseudo band gaps. Photoluminescence measurements reveal modification of emission by the photonic crystal consistent with angular dependent specular reflectance measurements. These results reveal a flexible and convenient route for fabricating high performance photonic crystal structures and optical microcavities.

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**1 Introduction** In the late 1980's the work of John [1] and Yablonovitch [2] began an extensive research interest in the modeling, fabrication, and testing of a new class of materials, "photonic crystals". A photonic crystal (PC) is a one, two or three-dimensional periodic structure comprised of alternating regions of high and low dielectric material, which cause the formation of "Photonic Band Gaps" (PBG's) within which radiation is not allowed to propagate. Consequently, a gap in the electromagnetic density of states (EMDOS) opens within a given frequency range.

The incorporation of microcavity defects into the photonic crystal provides the opportunity to create defect states within the PBG, allowing formation of a narrow emission line. Thus, photonic crystals and defects within them offer improved control over the generation and emission of light. Luminescent two & three dimensional PC microcavity structures have the potential for controlling the wavelength, luminosity, efficiency, time response and threshold properties by embedding a defect in a photonic crystal structure.

Different PC structures have been examined [3–6] by numerous groups and a complete photonic band gap has been demonstrated at millimeter [3] and infrared [5–7] wavelengths. The PC based on infiltration of synthetic opals has been established as one of the most promising methods for obtaining the desired periodic structure [6–11]. In this work, we report results of characterization of luminescent ZnS:Mn inverse opal films fabricated using Atomic Layer Deposition (ALD).

**2 Experimental** For this study, self-assembled oriented, face centered cubic (FCC) silica opal templates were formed on quartz and silicon substrates by sedimentation of monodispersed colloidal silica in confinement cells similar to the method of Park et al. [12], as described elsewhere [10]. The resulting

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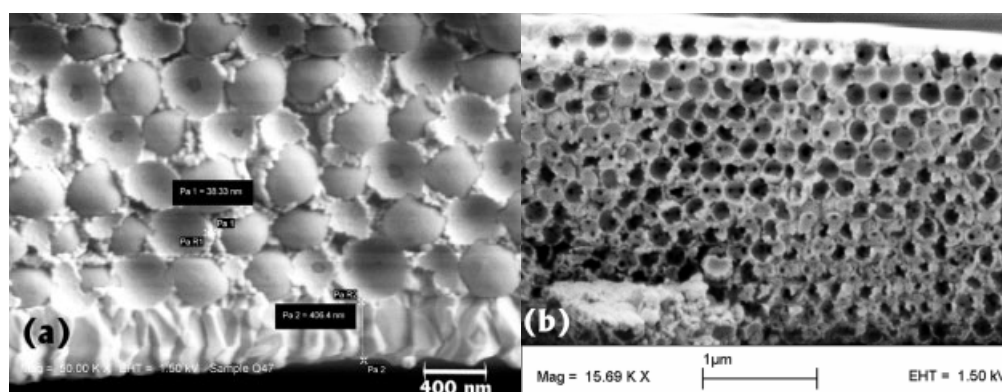
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opal films were 10  $\mu\text{m}$  thick, polycrystalline ( $\sim 100$   $\mu\text{m}$  grain size), and oriented with the (111) planes oriented parallel to the substrate; typical for confinement cell opals [13]. The interstitial volume of the opal was next filled with ZnS:Mn using conventional ALD precursors as we have reported previously [10]. Filling fractions of 95% were routinely attained, as calculated from resulting Bragg peak shifts.

ZnS was used as a prototype material because when doped it is highly luminescent with a wide range of emission wavelengths and it is also a well-studied material for ALD. However, its refractive index is too low ( $\sim 2.5$ ) for the formation of a full photonic band gap but high enough to produce a pseudo-photonic band gap (PPBG). Etching the infiltrated films in a 2% HF solution resulted in the removal of the silica spheres, and the formation of inverse opals.

The films were characterized using specular reflectivity, Scanning Electron Microscopy (SEM), and photoluminescence (PL) both after infiltration and after etching. For PL, the excitation was incident on the substrate at  $\sim 60$  degrees from normal, and the signal was collected using a fiber optic probe positioned at the desired angle relative to the substrate. Energy band diagrams for the sintered, infiltrated and inverse opals were calculated using the plane wave expansion method [14].

**3 Results** Successful infiltration and inversion was confirmed using SEM. The opals were viewed before and after infiltration, as well as after etching. To facilitate observation of the opal cross-section, the substrates were cleaved and the films were examined on edge as shown in Fig. 1. The image of the infiltrated opal shows that ZnS:Mn penetrates the opal and coats the  $\text{SiO}_2$  spheres conformally. In the second image, the silica spheres have been removed, leaving the ZnS:Mn inverse opal as a free standing structure.

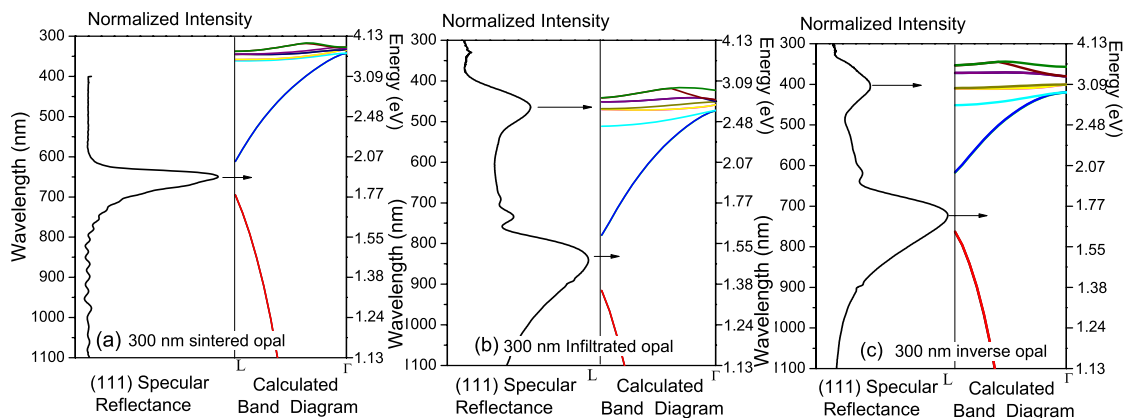


**Fig. 1** SEM images of cross sections of, (a) 460 nm infiltrated opal, and (b) 220 nm inverse opal.

The reflectance at normal incidence probes the band structure for the  $\Gamma - L$  direction in the PC. The reflectance spectra therefore contain peaks that arise due to the existence of PPBGs in the measured directions.

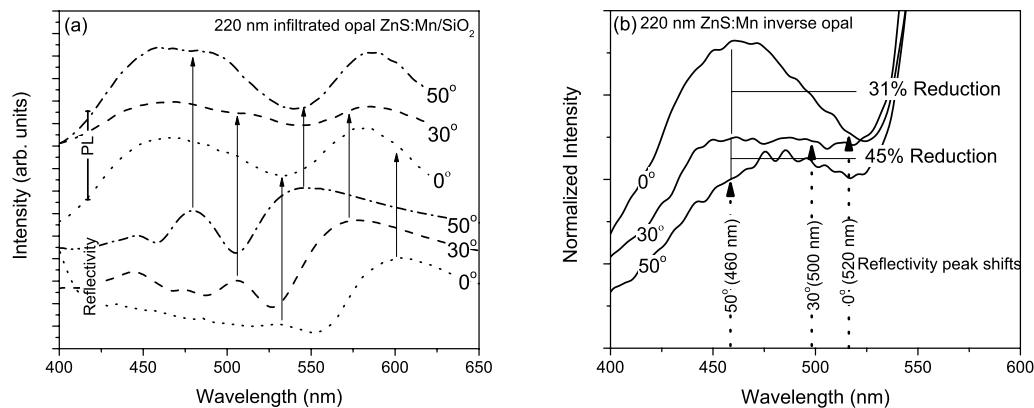
Figure 2 shows the measured normal incidence specular reflectance for a 300 nm opal prior to infiltration (sintered opal), after infiltration, and after etching (inverse opal), and the calculated band diagrams for each condition. The low energy pseudo band gap in the  $\Gamma - L$  band diagram corresponds to the peak that arises due to Bragg diffraction from the (111) planes. This peak position depends on several factors: sphere size, refractive index of the ZnS:Mn and of the silica spheres, and the ZnS:Mn filling fraction.

The reflectivity for the sintered opal shows a strong narrow peak at  $\sim 650\text{nm}$ , consistent with the gap shown in the band diagram for a 300 nm opal. After infiltration, the primary peak shifts to  $\sim 850\text{nm}$  and widens, also consistent with the calculated diagram. In addition, higher energy peaks are observed that coincide with the upper level bands where a PPBG is starting to form. For the inverse opal, the primary peak position decreases to  $\sim 725$  nm and becomes more sharply defined. Again, higher energy peaks are present; this time coincident with a definite PPBG.



**Fig. 2** Specular reflectance of 300 nm (a) sintered (b) infiltrated and (c) inverse opals, compared to their calculated band diagrams.

The angular dependence of the specular reflectance was also characterized. In a perfect opal, this would probe the band structure along a specific  $k$ -direction as determined by the angle of incidence and average refractive index of the structure. However, due to the polycrystalline nature of the opal films, measurement along off normal directions cannot be correlated with any one direction in the Brillouin zone. The measurements are simultaneous probes of all directions in the PC that are at the collection angle ( $\theta$ ) from the  $\Gamma - L$  direction. Thus, the angular dependent reflectivity spectra contain peaks due to PPBGs from several orientations, and are an average of all the directions.



**Fig. 3** Angular dependent PL of 220 nm opal, (a) infiltrated, and (b) inverse, showing comparison with the reflectivity measurements.

The angular dependent reflectivity spectra for the infiltrated opal are shown in Fig. 3a, for  $\theta = 0^\circ, 30^\circ$ , and  $50^\circ$ . The primary peak shifted from  $\sim 600$  nm to  $\sim 575$  nm for  $30^\circ$ , and to  $\sim 540$  nm for  $50^\circ$ . A secondary peak was found at 510 nm for  $30^\circ$ ; this peak doubled in magnitude and shifted to 480 nm, at  $50^\circ$ .

The reflectivity for the inverse opal exhibited a similar trend as the infiltrated opal with the primary peak shifting from 520 nm to 500 nm as  $\theta$  increased from  $0^\circ$ – $30^\circ$ . However, as  $\theta$  was increased to  $50^\circ$ , the largest peak ( $\sim 460$  nm) was shifted significantly more than would be expected for the (111) peak, indicating it most probably has a different origin. The positions of the largest reflectivity peaks are shown in Fig. 3b for the inverse opal.

Figures 3a and 3b show the angular dependent PL for the infiltrated and inverse opals, respectively. Typically, ALD grown ZnS:Mn infiltrated opals have PL peaks at 460 (Cl<sup>-</sup> defect) and at 585 nm (Mn<sup>2+</sup>), as reported previously [10]. The reflectivity spectra or peak positions are shown in the figures for comparison, indicating the locations of PPBGs.

In the PL curves shown for the infiltrated opal, the intensity of the 585 nm peak was reduced when  $\theta$  was shifted to 30°, which is consistent with the shifting of the PPBG on top of the peak as seen in the reflectivity. When the angle was increased to 50°, the effect on the PL is consistent with the shift of the (111) pseudo-PBG to 540 nm, as the valley at this wavelength is noticeably deeper. Also at 30°, the PL shows a dip that lines up with the 510 nm PPBG. The dip in the PL shifts to ~460 nm for  $\theta = 50^\circ$ , and again is coincident with the PPBG found from the reflectivity measurements.

For the inverse opal, the (111) reflectivity peak indicates that the pseudo-PBG is at a lower wavelength, so the 460 nm peak PL is expected to be affected, which is exactly what was observed. At  $\theta = 0^\circ$ , the reflectivity peak is between the 460 and 585 nm PL peaks, so no modification was observed. However, as the angle was increased to 30° the pseudo-PBG shifted on top of the 460 nm peak, and as a result, a 31% reduction in the normalized peak height was observed. The 50° measurement shows an additional reduction resulting in an overall 45% reduction in normalized peak intensity at 460 nm.

**4 Conclusion** The potential for luminescence wavelength control, efficiency enhancement, threshold reduction and improvement of other fundamental phosphor properties makes photonic crystals an exciting new research area. This work demonstrates successful formation of PPBGs in ZnS:Mn infiltrated and inverse opals as characterized by reflectivity and PL measurements, and the potential of ALD as a flexible and convenient route for the fabrication of high performance photonic crystals, particularly inverse opal structures, where very high infiltrations have been achieved.

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